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Integrated Ferroelectrics for Sensor and Capacitor Applications

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Ferroelectric materials have a unique range of properties such as high dielectric constant, pyroelectricity and piezoelectricity, which have enabled a host of diverse applications to be realized. The combination of ferroelectric materials as thin film with the developing field of micromachining has led to new and novel device applications. Although there are several routes available for thin film fabrication, e.g: Solution, MOCVD, etc., the solution approach in particular appeals as a simple process compatible with existing semiconductor processing equipment. This approach offers a route to low cost wafer scale fabrication, with potential for improved performance. At GMIRL, materials compositions within the PZT ($PbZr_xTi_{1-x}O_3$) solid solution system have been systematically investigated using a modified spin-coating deposition method, for applications in 2-D uncooled pyroelectric arrays and in MCM-D decoupling capacitors. In addition, use of the techniques of X-ray diffraction (XRD), Auger Analysis (AES) and Transmission and Scanning Electron Microscopy (TEM/STEM) has given considerable in-sight into structure determination, film homogeneity, and formation activation energy for the PZT (30/70) composition in particular.

Key Words: Ferroelectric; Thin Films; Solution; Pyroelectric; Capacitors.

Ferroeléctricos integrados para aplicaciones de sensor y condensador

Los materiales ferroeléctricos poseen un rango único de propiedades tales como alta constante dieléctrica, piroelectricidad y piezoelectricidad, que hacen posible diversas aplicaciones. La combinación de materiales ferroeléctricos en forma de lámina delgada dentro del campo emergente del micromecanizado han producido nuevas y novedosas aplicaciones. Aunque hay distintas rutas disponibles para la fabricación de láminas delgadas, la vía de solución se presenta como el proceso más simple, compatible con el equipamiento de procesado existente para semiconductores. Esta ruta ofrece una escala de fabricación de obleas de bajo coste, con un potencial de funcionamiento mejorado. En GEC-Marconi Infra-Red Limited, los materiales con composiciones dentro de las soluciones sólidas de PZT ($PbZr_xTi_{1-x}O_3$) se han estudiado sistemáticamente utilizando un método de deposición de recubrimiento por rotación modificado, para aplicaciones de matrices piroeléctricas 2-D sin refrigeración y en condensadores desacoplados MCM-D. Adicionalmente, la utilización de técnicas, de Difracción de Rayos X (DRX), espectroscopia Auger y microscopía electrónica de transmisión y de barrido (TEM, STEM) han proporcionado considerables aspectos a destacar sobre la determinación de la estructura, homogeneidad de la película, y energía de activación de la formación para la composición PZT (30/70) en particular.

Palabras clave: Ferroeléctrico, lámina delgada, solución, piroeléctrico, condensador

1. INTRODUCTION

Ferroelectric materials are characterized by the existence of a spontaneous remanent electric polarization that can be switched between two stable states by an applied electric field. In addition the polarization is sensitive to, or can influence, temperature (pyroelectric), stress (piezoelectric) or light (electro-optic). As a consequence of these properties there are many established sensor, actuator, transducer, capacitive that make use of bulk ferroelectric componentry available in the marketplace today. Such device structures are nearing the end of their development potential and the next generation will be fully integrated structures where the ferroelectric material is formed as a thin film directly onto the semiconductor part of the device. This brings benefits in miniaturization, wafer scale manufacture, reduced cost and higher sensitivity. This paper will summarize briefly the applications of thin film ferroelectrics to two such device test structures. The deposition and microstructural properties of our preferred ferroelectric material are then described.

1.1. Integrated Pyroelectric Detector Arrays

There is a growing interest in the sensing of long wavelength infrared (IR) radiation, in particular for imaging applications. To date, the majority of such sensors have been photon detectors, using semiconductors cooled to liquid N_2 temperatures. As an alternative, pyroelectric thermal detectors offer the possibility of simpler devices, not requiring cooling, giving sensitive detection in the 8-14 μm wavelength band, which corresponds to a window in the atmosphere absorption of IR radiation. There have been several reports on imaging arrays using pyroelectric ceramics (1-3), which are all refractory oxides with the perovskite type lattice structure. The principle of a pyroelectric detector is depicted in Fig. 1. Essentially, the incident infrared radiation absorbed in the pyroelectric material causes a small temperature change resulting in a displacement of electric charge which is sensed by the amplifier of the readout circuit.

To date, practical arrays have largely been based upon the interfacing of bulk ferroelectric ceramic materials (1) with

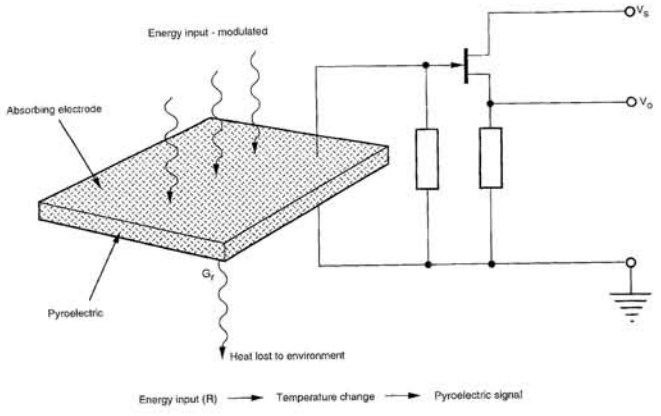

Fig. 1. *Principal of a pyroelectric detector.*

CMOS readout circuits using flip-chip technology. However, there has also been significant effort in developing techniques for directly integrating pyroelectric thin films with silicon IC (4). The performance of the thermal imaging array is dependent on the pyroelectric material which has a figure of merit defined as:

$$F_D = \frac{P}{Cv\sqrt{\varepsilon\varepsilon_o \tan\delta}} \qquad [1]$$

where P is the pyroelectric coefficient, C_v is the volume specific heat, ε is the dielectric constant of the ferroelectric, and tan δ is the dielectric loss of ferroelectric.

F_D is proportional to the signal-to-noise ratio of the detector when the noise term is dominated by the Johnson noise associated with the detectors AC conductance.

A number of simple targets can be quantified for a sensitive detector:

i. A low thermal conductance from the detector element to the substrate, by suitably supporting the pyroelectric element as shown in Fig. 2.
ii. A reduction of the element thickness, for low heat capacity.
iii. An efficient absorber is required.
iv. A low temperature film deposition process for reduced damage to the silicon CMOS circuitry.
v. A good pyroelectric material, as measured by a single F_D.

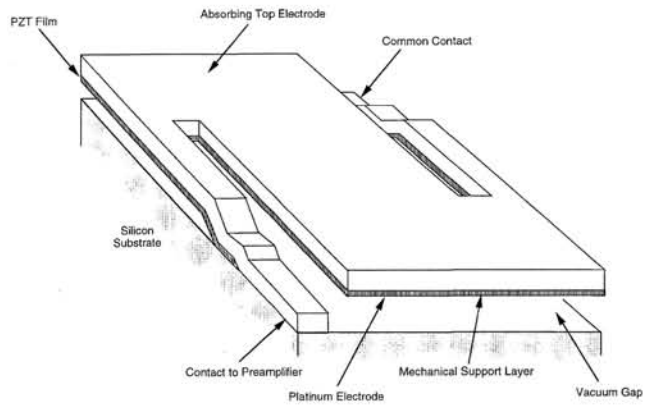

Fig. 2. *Schematic of a micromachined integrated pyroelectric element.*

For commercial bulk PZT based ceramic produced at GMIRL, P is of the order of 4 x 10^{-4} $Cm^{-2}K^{-1}$, and $F_D \approx 4 - 5 \times 10^{-5}$ $(Nm^{-2})^{-0.5}$. The PZT films as deposited have some pyroelectric response prior to poling, though the sign of the coefficient varies with composition. Assuming a $C_v = 2.7 \times 10^6$ $Jm^{-3}K^{-1}$, the measured F_D is 2 x $10^{-5}(Nm^{-2})^{-0.5}$, which is similar to the values obtained in bulk undoped ceramic for this system. For a more comprehensive account the reader is referred to reference. 5.

1.2. Thin film Capacitors

High performance decoupling capacitors are a critical part of integrated circuit systems and multichip modules (MCM). As the clock rates for MCM increase, suitable signal decoupling will be required since the inductance associated with interconnecting decoupling capacitors and IC's will limit operational frequency. One such strategy, is to integrate thin-film capacitors preferably embedding the capacitor into one of the interconnect layers (6). This approach has two potential advantages, firstly minimizing inductive parasitics, and secondly, reducing the size of the MCM. For such a requirement, materials deposited as thin films with high dielectric constants are specified, and possible candidates are the PZT family. Compared to DRAM (Dynamic Random Access Memory) applications, larger area capacitors are required placing extra emphasis on yield and leakage current. A schematic of the MCM-D (D - deposited) structure, including the decoupling capacitor is shown in Figure 3, and a photo of a completed MCM-D wafer is shown in Figure 4. A more detailed account of the processing and properties is given in Reference. 7.

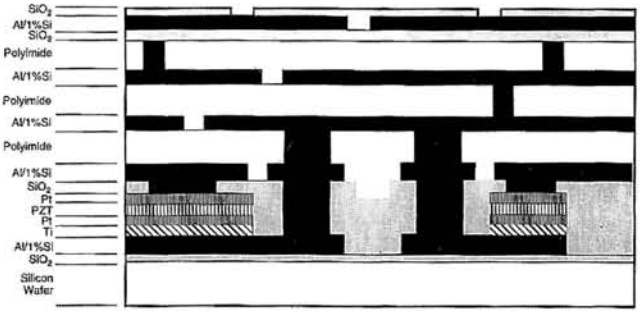

Fig. 3. *Schematic of a MCM-D structure, incorporating a thin film capacitor.*

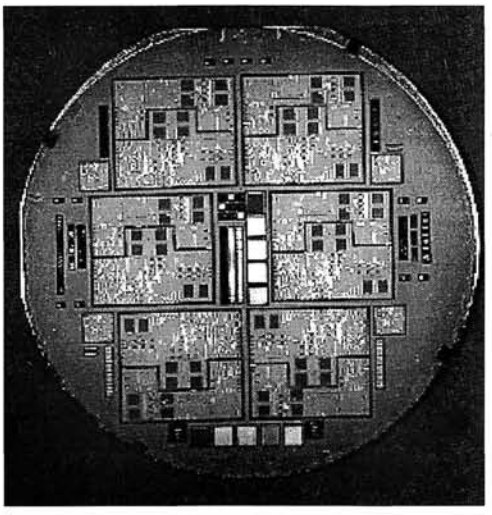

Fig. 4. *Photograph of a completed MCM-D wafer.*

2. PZT FILM DEPOSITION

A range of materials have been studied, for both the above applications, concentrating mainly on lead titanate and modifications to it (8). The most success has been gained with lead zirconate titanate (PZT) with a Zr/Ti ratio of 30/70 deposited from solution by spin coating. The deposition route has been reported in detail previously (8). The precursors are titanium n-butoxide and zirconium butoxide-butanol complex and lead acetate trihydrate in a 0.2M solution of 2-methoxyethanol, stabilized against hydrolysis with acetylacetone. This has been deposited on standard uniform silicon substrates, thermally oxidized and provided with a titanium/platinum bottom electrode. The process provides a dense film, at a rate of around 0.015μm/layer. Deposition over 6" diameter wafers has been demonstrated, with visually uniform, crack-free films over the full area.

3. FILM CHARACTERIZATION

Various techniques have been utilized to characterize the PZT thin films. It is often found that a combination of all is required to give a definitive view regarding the structure of the film.

3.1. Powder X-ray Diffraction

X-ray diffraction (XRD) studies has shown that the films tend to favor the (111) orientation, probably because of the close lattice match to the underlying (111) platinum electrode. With 510°C bakes single phase (111) material is produced, though at lower temperatures there is also some (100) orientation and increasing amounts of a FCC cubic pyrochlore second phase. Similarly, electrode thickness, with a thickness of at least 500Å gave single phase films, whereas multi-phase material is obtained on thinner electrodes. Recent studies have shown that the electrode surface «roughness» and magnitude of (111) orientation play a significant role in determining the PZT film orientation. The method of film baking also has a significant effect on orientation, for example, dual temperature bakes at 350° and 650°C tend to yield more multi-phase material.

3.2 Transmission Electron Microscopy

The crystallisation behavior of the PZT deposit into the desired perovskite phase is complicated and can be highly dependent on the processing conditions. Since the transformation is diffusional, the rate of transformation, *R*, may be expected to follow a law of the form

$$R = A \exp.\left(\frac{-E_{ac}}{kT}\right) \qquad [2]$$

where A is a constant with dimensions of nm s^{-1}, k is Boltzmann's constant and T is the absolute temperature (K). A film was produced by depositing to give a layer approximately 400nm thick, each of which was baked at 350°C for 120 s to drive off residual organic. The wafer was then diced into 4x4 cm squares, and each segment was annealed for varying times and temperatures. A typical TEM cross-section of a partly transformed film is shown in Fig. 5. The PZT films always transform from the bottom Pt electrode towards the top surface, and the columnar perovskite is readily distinguished from the overlying pyrochlore. The thickness of the perovskite layer was measured for each of the samples to give a measure of the transformation rate *R*. Two deviations from this microstructure were observed. First, 'rosettes' were occasionally seen in the upper part of the layer (Fig.5a). These rosettes appear to be formed by nucleation of the perovskite phase in the bulk of the film, and not from a nucleation site on the Pt. Interestingly, the lateral radius of the rosette is larger than the thickness of the columnar perovskite, indicating that the rosette either nucleated earlier, or grew faster, than the surrounding perovskite. Rosettes were observed even in fully transformed films. The second deviation from the normal microstructure was in the form of cracks in the pyrochlore (Fig.5b). These were found to be associated with the rosettes, either linking pairs or bunches of rosettes, or between rosettes. These probably arise from differences in thermal expansion of the pyrochlore and the perovskite rosettes upon cooling from the annealing temperature.

The measured transformation rate as a function of temperature, together with a fitted line of the form of, [2], is shown in Fig. 6. Ecuation [2] fits the data reasonably well, although there is some deviation from the line which is greater than the errors in the data. The activation energy is found to be 3.54±0.3 eV, and the pre-exponential factor is 2.6 $x10^{22}$ nm s^{-1}.

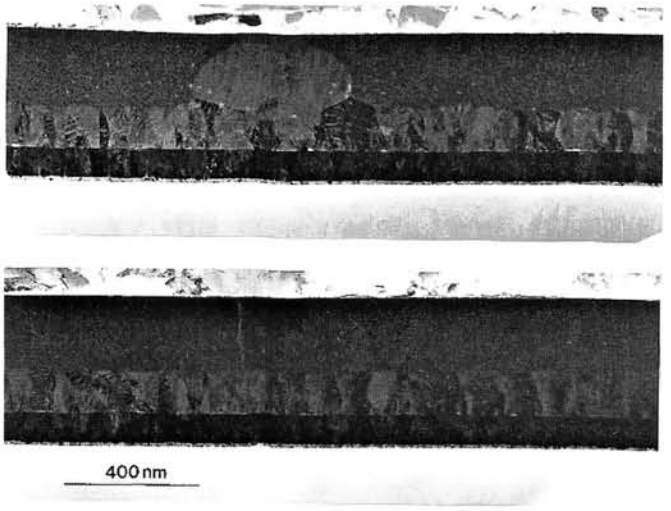

Fig. 5. *(a) SEM micrograph of a partly converted PZT film, showing «rosettes». (b) SEM micrograph showing cracking in the pyrochlore phase.*

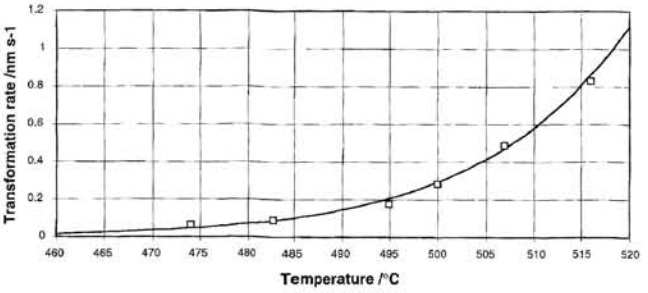

Fig. 6. *Plot of PZT pyrochlore-perovskite conversion rate.*

3.3. Auger Spectroscopy

Auger electron spectroscopy (AES) was conducted using a VG CLAM Hemispherical analyzer, with typical operating conditions of 7keV for the electron column; beam current of 0.1μA and sputtering with xenon at 2keV. Fig.7 is an AES depth profile taken through a 5 layer PZT film with columnar growth. The PZT, Pt, Ti and part of the SiO_2 layers are visible as the depth into the sample increases. It can be seen that Pb is enriched at the surface of the PZT film. The intensity of Pb decreases rapidly to half its surface value after the first etch period and does not change dramatically throughout the film thickness. Throughout the film thickness the level of oxygen remains relatively constant. Fluctuations in the Zr and Ti composition ratio through the film have been observed. This behavior is linked to a cyclic response arising from the variation in the Zr and Ti composition within a single layer. The average Ti concentration increases slowly from the outer PZT surface to the Pt electrode interface. In single layer films the Zr concentration steadily falls to a minimum at half the film thickness. However, in films with multiple layers the Zr drops to a minimum at the end of each layer.

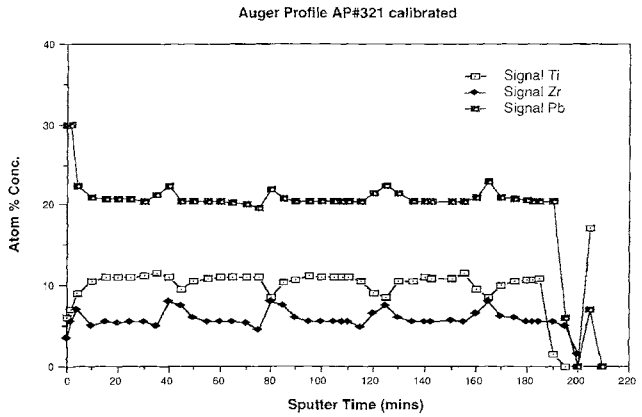

Fig. 7. *Auger depth profile through a PZT film, showing compositional variations.*

4. CONCLUSIONS

PZT (30/70) thin films on $Pt/Ti/SiO_2/Si$ substrates have been successfully produced at temperatures as low as 510 °C. Two application's, Uncooled Thermal Imaging and MCM-D Capacitors, in particular have been highlighted. XRD, TEM/STEM, and AES have been used to study the growth and microstructure of the films, especially of the interfaces. It has been shown that the films were highly (111) preferentially oriented single phase perovskite. PZT crystallisation initiated at the platinum surface, and the crystallites grow epitaxially through the sequentially deposited layers. A minority terminate at layer interfaces and new nucleation occurred at this interface. The activation energy for conversion to perovskite PZT was found to be 3.54±0.3 eV, and the pre-exponential factor is 2.6 $x10^{22}$ nm s^{-1}. Compositional variations are observed within each deposited PZT layer which are considered to be the source of the inter-layer contrast in TEM and are probably caused by Zr being swept before the crystallizing perovskite front.

5. ACKNOWLEDGMENTS

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